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Iridium Catalysis: Reductive Conversion of Glucan to Xylan

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By using iridium catalysed dehydrogenative decarbonylation, we converted a partly protected cellobioside into a fully protected xylobioside. We demonstrate good yields with two different aromatic ester protecting groups. The resulting xylobioside was directly used as glycosyl donor in further synthesis of a xylooctaose.

In the last decade a large contribution to glycobiology research and glycomics has been made through the extensive development of epitope-recognizing antibodies, carbohydrate-binding-modules and carbohydrate microarrays.¹ The construction of oligosaccharide microarrays, enzymatic studies and development of specific antibodies requires well-defined and pure oligosaccharides in reasonable quantities. These have traditionally been isolated from plant material following partial enzymatic and/or chemical degradation. However, the purity requirement results in a time-consuming purification process and often the resulting glycans are contaminated with closely related structures, which decrease their utility. For this reason, chemical synthesis currently offers a superior method for obtaining sufficient amounts of well characterized structures in high purity.²

The plant cell wall is the single largest source of sustainable biomass on the planet and efficient utilization of cell wall material will be one of the keys to realizing the biobased society of the future.^{3,4} Glucuronoarabinoxylan (GAX) is one of the major components of feedstocks that are utilized for the production of 2nd generation biofuels.^{3,4} GAXs are composed of a backbone of β -(1 \rightarrow 4)-D-xylopyranose, partially substituted by arabinosyl, glucuronic acid and 4-O-methyl glucuronic acid

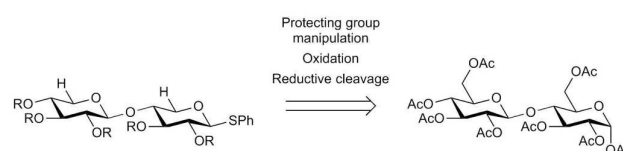


Figure 1 Creating xylobioside building blocks from cellobiose octaacetate.

residues.^{6,7}

Therefore, efficient methods to synthesize well-defined oligoxylans are important to these research areas. The β -1,4-xylosyl backbone has been targeted by different approaches. The first chemical synthesis of a xylan was achieved by Myhre and Smith,⁸ who synthesized xylobiose. Twenty years later, Kováč and Hirsch made a sequential synthesis of methyl xylotetraoside and xylohexaoside. Both groups employed glycosyl bromides as donors in a linear strategy.^{9–11} A synthetic blockwise approach was used by Takeo *et al.*, who obtained fully protected xylohexaose as a stepping stone towards xylodecaose,¹² and later accessed a whole series of xylans.¹³ More recently, several examples of enzymatic synthesis of xylans have emerged, however not on a larger scale.^{14–16} A powerful method for automated synthesis resulted in a broad range of oligoarabinoxylans and xylans made by Schmidt *et al.* as recently as 2015.¹⁷

We wanted to employ a xylobioside building block in order to speed up assembly of larger glycans. Rather than prepare the required disaccharide from xylose, we envisioned a route starting from protected cellobiose (Figure 1). This would offer several advantages as cellobiose octaacetate is readily available by acetolysis of cotton^{18,19} and commercially available in multi-gram amounts at low cost. Furthermore, the chemistry of glucose is well established and highly regioselective, rendering protecting group manipulations facile. By realizing a transformation from a hexose to pentose, we are accessing a xylobioside building block for oligosaccharide synthesis in a few steps.

A recent description of iridium catalyzed decarbonylation²⁰ and the knowledge of iridium complexes as excellent hydrogen transfer catalysts, inspired the development of homogeneous

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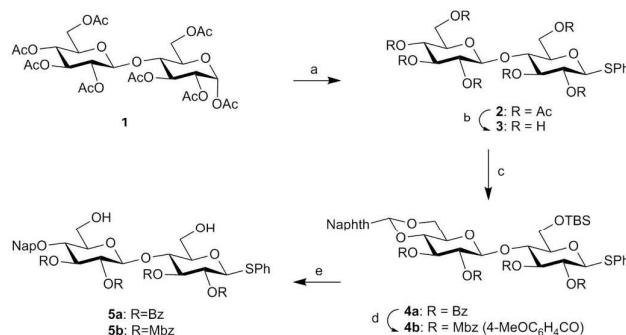
For details of the performed experiments and compound characterization, see the Electronic Supplementary Information (ESI) available: DOI: 10.1039/x0xx00000x

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tandem catalytic system.²¹ An iridium complex, generated in situ from [Ir(cod)Cl]₂ and racemic 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene (BINAP), promotes the catalytic dehydrogenation of a primary alcohol and a subsequent decarbonylation leading to release of hydrogen and carbon monoxide. A related sequence has also been achieved by Melnick *et al.*²² using stoichiometric amounts of an iridium (I) complex with a pincer ligand, bis(2-(diisopropylphosphanyl)-4-methylphenyl)amine converting ethanol into methane after photolysis of an intermediate Ir–CO complex. Additionally, Ho *et al.*²³ used a rhodium (I) complex with tris(4,4-dimethyl-2-oxazolinyl)phenylborate to perform photocatalytic dehydrogenative decarbonylation on a range of primary alcohols.²⁴ The reductive dehydrogenation-decarbonylation of carbohydrates to produce, for example, pentoses from hexoses has not previously been described. Therefore, we set out to investigate, if the protocol developed by Olsen and Madsen^{21,25} could be employed for this purpose.

The partially protected cellobiosides **5a** and **5b** were synthesized as shown in Scheme 1, starting from peracetylated cellobiose (**1**) that was converted to the thiophenyl glycoside via the bromide.²⁶ The sequence afforded the desired thio β-D-cellobioside **2** in a high yield. After deacetylation using Zemplén conditions, the resulting thiophenyl cellobioside **3** was selectively protected with 2-naphthylidene, TBS and benzoates to give the fully protected cellobioside **4a**. The acetal and silyl protecting groups are orthogonal, however, the optimized order of unmasking the primary alcohols was selective acetal opening prior to desilylation, which afforded the partly protected cellobioside **5a** in 85% yield. When the order was reversed the product was obtained in a mere 23%. The corresponding 4-methoxybenzoylated cellobioside **4b** was obtained by debenzoylation of **4a** with NaOCH₃ in CH₃OH, followed by treatment with 4-methoxybenzoyl chloride. The product was subjected to identical conditions to give the 4-methoxybenzoylated cellobiose **5b**.

The dehydrogenative decarbonylation was initially investigated for **5a** (Figure 2).²¹ Early optimization showed that performing the reactions under a slow flow of argon (as opposed to simply



Scheme 1 Synthesis of the partially protected cellobiosides **5a** and **5b**. a) (i) HBr, AcOH, Ac₂O, (ii) thiophenol, Na₂CO₃, TBAHSO₄, H₂O/CH₂Cl₂ 72% (2 steps); b) NaOCH₃, CH₃OH, quant.; c) (i) 2-naphthaldehyde, CH(OCH₃)₃, 10 mol % pTSA-H₂O, CH₃CN, 60 °C, (ii) TBSCl, DMAP, py, 0→22 °C, (iii) BzCl, DMAP, py, CH₂Cl₂, 0→23 °C, 70 % (3 steps); d) (i); NaOCH₃, CH₃OH/CH₃CN, 60 °C, (ii); MbzCl, DMAP, Et₃N, py, CH₂Cl₂, 0→22 °C, 68 % (2 steps); e) (i) BH₃·THF, 20 mol % Cu(OTf)₂, CH₂Cl₂, 0→22 °C, (ii) HF (aq), CH₃CN, 22 °C, 85 % (2 steps, **5a**), 48 % (2 steps, **5b**).

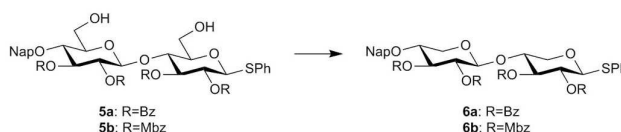


Figure 2 Dehydrogenative decarbonylation resulted in successfully converting partly protected cellobioside **5a** and **5b** to fully protected xylobiosides **6a** and **6b**.

refluxing under argon atmosphere) greatly enhanced the reaction rate and gave the product in 30% yield. We presume this can be ascribed to a more efficient removal of carbon monoxide and/or hydrogen during the reaction. A set of experiments were conducted to investigate the effect of adding hydrogen scavengers (Table 1). Diphenylacetylene and styrene both improved the yield of the reaction compared to not having a scavenger (entries 1–3). Norbornene is an unsaturated, bridged cyclic hydrocarbon and since strain is released upon saturation, norbornene is an excellent candidate for hydrogen scavenging.^{22,27} It was added in different equivalents and we observed a clear effect of the additive (entries 4–6). A positive effect was obtained with 1.2 and 2.2 equiv. of norbornene as hydrogen scavenger, but when 4.4 equiv. were used the yield dropped significantly. After establishing norbornene for optimal hydrogen scavenging, a range of parameters were screened (Table 2). Performing the reaction in diglyme, a high boiling polar aprotic solvent, had in some cases improved decarbonylation reactions,^{20,28,29} but in our case no conversion of **5a** was observed (entry 1). Co-solvents such as *N,N*-dimethylacetamide (DMA) have been reported to stabilize catalytic decarbonylation reactions.²⁹ Nevertheless, performing the reaction in a 1:9 mixture of DMA and mesitylene (entry 2), did not improve the reaction time nor the yield. By lowering the reaction temperature by refluxing in *m*-xylene (boiling point 139 °C, entry 3), we expected prolonged reaction times and less product decomposition. The result, however, was a reduction in reaction yield to merely 16%. In fact, performing this reaction in toluene (boiling point 110 °C) for more than 3 days did not show any significant conversion. Originally, Olsen and Madsen²¹ found mesitylene to be the best solvent for the reaction and observed more consistent results when it was saturated with H₂O. This was also the case for substrate **5a** (Table 2, entries 4–6), which emphasizes that trace amounts of water are beneficial to the reaction. Addition

Table 1 The effect of additives on the dehydrogenative decarbonylation. a

Entry	Scavenger	Equivalents ^b	Yield (%) ^c
1			30
2	Diphenylacetylene	2.2	43
3	Styrene	2.2	43
4	Norbornene	1.1	41
5	Norbornene	2.2	48 ^d
6	Norbornene	4.4	23

^a Reactions were performed by *in situ* generation of the catalyst, using 15 mol % [Ir(cod)Cl]₂ and 30 mol % (*rac*)-BINAP. The reactions were performed at reflux in mesitylene and stopped after 16 hours, when TLC indicated full conversion of **5a**. ^b Relative to the amount of disaccharide **5a**. ^c Isolated yield of **6a**. ^d Average of two reactions.

of LiCl has been shown to increase the reaction rate, but that was not the case for **5a**, instead the yield dropped significantly (entry 7).

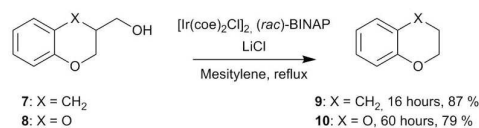
When potassium chloride with crown ether was added to produce more accessible chloride ions the yield improved, however not to the levels obtained without additive (compare entry 8 with entries 5 and 6).

The dehydrogenative decarbonylation protocol²¹ originally used achiral substrates, hence no difference in performance was expected using the two different antipode of the ligand. As the substrate has multiple stereocenters, we tested both antipodes of BINAP and observed a significant difference in catalytic efficiency (entries 9 and 10). (*R*)-BINAP (entry 9) resulted in more than twice the amount of isolated product compared to (*S*)-BINAP (entry 10), however, the reaction with (*R*)-BINAP was still lower yielding than when using the racemic ligand (entry 6). Madsen and co-workers showed that the reaction operates through two coupled catalytic cycles (see also Supporting Information).³⁰ We hypothesize that either the two antipodes of BINAP have different efficiency in the two cycles or alternatively that the iridium complexes formed from each enantiomer matches up differently with the two molecules of glucose in cellobiose, as they represent different chiral environments. The latter would help explain why complexes formed from the racemic ligand had the best overall efficiency. This is also in agreement with the main byproducts observed, resulting from a single chain shortening (Glu-Xyl and Xyl-Glu disaccharides, see Supporting Information). Reducing the catalyst loading to 15 mol % gave a lower isolated yield (entry 11), but an increase to 60 mol %

resulted in a faster reaction without a significant improvement in the yield (entry 12). When the concentration of the reactions was varied with fixed times, a significant influence on the outcome was observed (entries 13–16). The isolated yields were diminished at lower concentrations (entries 13 and 14), and this effect was even stronger when concentrations were increased (entries 15 and 16). Furthermore, TLC analysis during the reactions showed more decomposition when concentrations were above 0.1 M. The optimized reaction conditions were applied to the 4-methoxybenzoylated cellobioside **5b** giving an acceptable 37% yield (entry 17).

As a general observation, longer reaction times did not promote higher yields, even though intermediate products are converted continuously. One reason could be decomposition: in a qualitative experiment, a sample of starting material and one of product were heated in mesitylene and monitored by TLC, which revealed a slow, but steady decomposition, more pronounced for the product than for the starting material. When scaling up the reaction we initially observed a dramatic decrease in yield; however, this was solved by performing a thorough degassing by freeze-pump-thaw prior to heating and formation of the active complex. In this manner, we obtained an effective reaction on up to a five-gram scale affording the same result as the 200 mg entries shown in Table 2.

Interestingly, substrates with neighboring endocyclic oxygen were previously shown to react more slowly by Olsen.²⁵ This effect was clearly visible when compound **7** and **8** were subjected to dehydrogenative decarbonylation (Scheme 2). The pronounced effect of the endocyclic oxygen on the reaction rate compared to the methylene adduct, leads us to hypothesize that the endocyclic oxygen can coordinate to iridium, stabilizing a catalytic intermediate and thus negatively impact the kinetics of the reaction. Subjecting a 2,3,4-tribenzoylated methyl glucoside to the same reaction conditions resulting in the corresponding methyl xyloside in 13% yield, together with 48% of a byproduct, where the 4-*O*-Bz group had migrated to the 6-position of glucose (not shown). With the thio-xylobioside **6a** in hand, a reducing end building block for oligoxylan assembly was prepared by coupling to benzyl alcohol, which gave the benzyl β -xylobioside in 55%, along with the α -adduct in 17% yield (Scheme 3). The Nap group was removed with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), affording acceptor **11a** in a near quantitative yield (98%). Coupling with **6a** required NIS in combination with TfOH and resulted in the xylotetraoside in a moderate yield,



Scheme 2 Dehydrogenative decarbonylation of substrates with and without adjacent endocyclic oxygen.¹⁵ Using 2.5 mol% [Ir(cod)Cl]₂, 30 mol % (*rac*)-BINAP, 10 mol % LiCl and H₂O saturated mesitylene.

which was readily deprotected with DDQ to give acceptor **12a**. When **12a** was subjected to glycosylation conditions with the thio-xylobioside **6a**, we observed no conversion of the

Table 2 Optimization of conditions for formation of **6a** from **5a**.^a

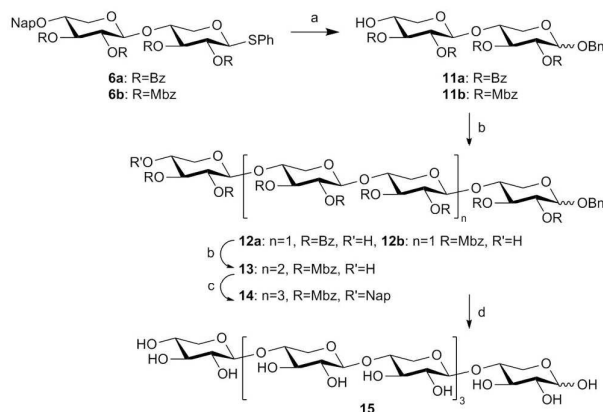
Entry	Solvent	Conc. (M) ^b	Time (h) ^c	Yield (%) ^d
1	Diglyme	0.1	72	No conv.
2	Mesitylene/DMA (1:9)	0.1	28	19
3	<i>m</i> -Xylene	0.1	26	16
4	Mesitylene (<i>dry</i>)	0.1	19	28
5	Mesitylene (untreated)	0.1	16	48
6	Mesitylene (H ₂ O sat.)	0.1	17	47
7 ^e	Mesitylene (H ₂ O sat.)	0.1	23	30
8 ^f	Mesitylene (H ₂ O sat.)	0.1	16	39
9 ^g	Mesitylene (H ₂ O sat.)	0.1	22	37
10 ^h	Mesitylene (H ₂ O sat.)	0.1	22	14
11 ⁱ	Mesitylene (H ₂ O sat.)	0.1	48	31
12 ^j	Mesitylene (H ₂ O sat.)	0.1	4	51
13	Mesitylene (H ₂ O sat.)	0.01	16	17
14	Mesitylene (H ₂ O sat.)	0.05	16	30
15	Mesitylene (H ₂ O sat.)	0.2	16	28
16	Mesitylene (H ₂ O sat.)	0.5	16	Traces
17 ^k	Mesitylene (H ₂ O sat.)	0.1	16	37

^a Reactions were performed by in situ generation of catalyst, using 15 mol% [Ir(cod)Cl]₂, 30 mol % (*rac*)-BINAP and 2.2 equiv. norbornene.

^b Concentration of disaccharide. ^c The reactions were performed at reflux in mesitylene and stopped, when TLC indicated full conversion or no further development. ^d Isolated yields. ^e 60 mol% LiCl. ^f 30 mol% KCl, 18-crown-6. ^g (*R*)-BINAP, instead of (*rac*)-BINAP. ^h (*S*)-BINAP, instead of (*rac*)-BINAP. ⁱ 7.5 mol % [Ir(cod)Cl]₂ and 15 mol % (*rac*)-BINAP. ^j 30 mol % [Ir(cod)Cl]₂ and 60 mol % (*rac*)-BINAP. ^k Disaccharide **5b**.

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Scheme 3 The obtained donors were used in glycosylation reactions to synthesize fully protected oligoxylans. (a); for **6a**; (i), BnOH, NIS, 10 mol% TMSOTf, CH₂Cl₂, (ii) DDQ, 1:9 H₂O/CH₂Cl₂, 54 % (2 steps); for **6b**; (i), BnOH, NIS, 20 mol% TfOH, 4 Å MS, CH₂Cl₂, (ii) DDQ, 1:9 H₂O/CH₂Cl₂, 79 % (2 steps); (b); for **12a**; (i), **6a**, NIS, 2.5 mol% TfOH, 4 Å MS, CH₂Cl₂, (ii) DDQ, H₂O/CH₂Cl₂ (1:9), 60 % (2 steps); for **11b**; (i), **6b**, NIS, 20 mol% AgOTf, 4 Å MS, CH₂Cl₂, (ii) DDQ, H₂O/CH₂Cl₂ (1:9), 89 % (**12b**, 2 steps), 74 % (**13**, 2 steps); (c); **6b**, NIS, 20 mol% AgOTf, 4 Å MS, CH₂Cl₂, 71 %; (d); (i), NaOCH₃, CH₃OH/THF (1:5); (ii), H₂ (g), Pd/C, H₂O/THF (1:2), 23 % (2 steps).

acceptor and only hydrolyzed donor and unreacted acceptor was recovered. Despite numerous attempts, we were unable to optimize the reaction to produce more than trace amounts of product and we ascribe this to a mismatch between the xylo-tetraoside acceptor and the biose donor.

Instead, we turned to donor **6b**, carrying 4-methoxybenzoyl protection. Through a similar sequence of reactions, we could very rapidly access the benzyl xylo-tetraoside (**12b**), –hexaoside (**13**) and –octaoside (**14**) in very good yields. This example highlights the importance of protecting groups in carbohydrate chemistry, as they clearly have a profound impact on reactivity in this case. Finally, the fully protected benzyl xylo-octaoside **14** was globally deprotected by Zemplén deesterification followed by hydrogenolysis, affording octasaccharide **15** after purification by size exclusion chromatography.

In conclusion, we successfully accomplished the conversion of partly protected cellobiose to xylobiose. This is the first example of a 1-pot reaction forming pentoses from hexoses, and **6b** was directly used as glycosylation donor in the synthesis of xylans **12–14**. The iridium-catalyzed dehydrogenative decarbonylation proved to be a robust method also on a gram scale. Meticulously degassing prior to reaction was crucial to obtaining good yields when scaling up.

Acknowledgements

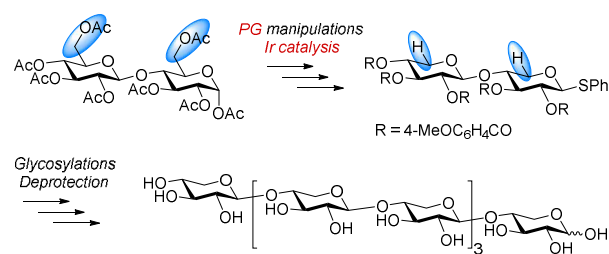
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Conflicts of interest

There are no conflicts to declare.

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Iridium catalyzed dehydrogenative decarbonylation is used to convert cellobiosides to xylobiosides, which is used in rapid assembly of oligoxylans.